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GROWTH AND CHARACTERIZATION OF ZINC SULFIDE FILMS BY CONVERSION OF ZINC OXIDE FILMS WITH H_2S

by

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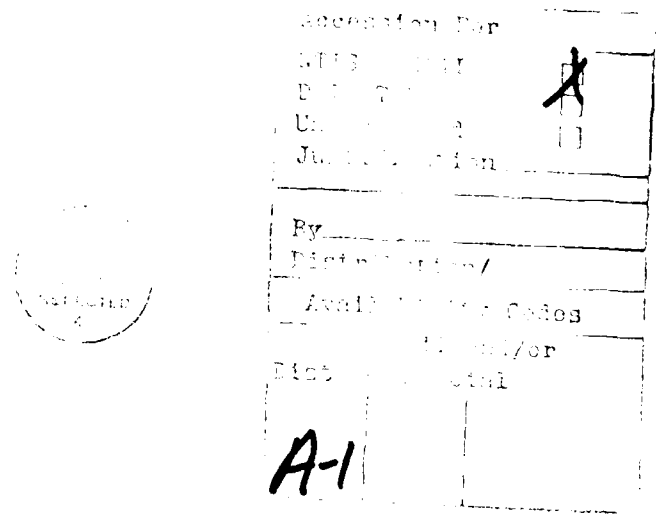

GROWTH AND CHARACTERIZATION OF ZINC SULFIDE FILMS BY CONVERSION OF ZINC OXIDE FILMS WITH H_2S

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ABSTRACT

Zinc sulfide films were prepared by conversion of zinc oxide films in the presence of hydrogen sulfide. The films which contained both the hexagonal and cubic forms of zinc sulfide were shown to be uniform and gave a measured band gap of 3.65 eV.
MATERIALS INDEX: Zinc, Oxides, Sulfides

Introduction

Zinc sulfide is an IR window material and a transparent semiconductor with a large direct band gap. It also possesses piezoelectric, photoconductive and electroluminescent properties. Thin films of zinc sulfide can be utilized for infrared antireflection coatings, light-emitting diodes (LEDs), electroluminescent (EL) displays, multilayer dielectric filters, optical phase modulation and light guiding in integrated optics. In recent years, there has been a large amount of effort directed at the growth of high quality films of ZnS. Various fabrication techniques have been employed, such as ion beam sputtering (1), atomic layer epitaxy (ALE) (2), molecular beam epitaxy (MBE) (3), metal-organic chemical vapor deposition (4) and spray pyrolysis (5).

Recently, a novel ultrasonic nebulization and pyrolysis method has been developed in this laboratory (6). High quality films of zinc oxide can be grown using this simple technique. Previously, Maruska (7) reported the conversion of CdO films to CdS films by an ion exchange process. It therefore appeared feasible to convert ZnO films with H_2S into ZnS films.

Experimental

Preparation of zinc sulfide films

Zinc sulfide films were prepared by sulfurization of zinc oxide films with hydrogen sulfide. Zinc oxide films on silicon and silica substrates were prepared by ultrasonic nebulization of zinc acetate solutions and thermal conversion of the zinc acetate to zinc oxide films. The detailed procedure has been described elsewhere (8). Zinc oxide films as deposited were annealed in a mixture of hydrogen sulfide and argon (H_2S:Ar = 1:1) in a horizontal tube furnace. The flow rate of the gas mixture was 50 cc/min. The temperature of the furnace was raised gradually from room temperature to 500°C in 4 hrs. The furnace was maintained at 500°C for another 3 hrs and then cooled down slowly in the H_2S/Ar atmosphere. Completion of the conversion was verified by x-ray diffraction analysis and infrared spectroscopy of the films.

Characterization

The thickness of zinc sulfide films on silicon substrates was determined by ellipsometry using a Rudolph Research Auto El-II ellipsometer. X-ray diffraction patterns of the films were obtained using a Philips diffractometer and monochromated high intensity $CuK\alpha_1$ radiation (λ = 1.5405Å). Diffraction patterns were taken with a scan rate of 1° 2θ/min over the range 12° < 2θ < 80°. The surface topography of the films was studied by scanning electron microscopy. Pictures were taken with an Amray 1000A Scanning Electron Microscope operating at 20 KV. Semi-quantitative (SQ) EDS analysis was performed on the JEOL 840 SEM with an electron beam energy of 20 keV. Spectra were analyzed on the TN5400 using the SQ program, which calculates the k-ratios from stored elemental standards.

Optical measurements of the films on silica substrates were performed using a Cary Model 17 dual beam ratio recording spectrophotometer in the range of 300 nm to 1500 nm. The optical band gap was determined from the transmittance near the absorption edge. Infrared spectra at room temperature were obtained on a Perkin-Elmer 580 single-beam scanning infrared spectrophotometer at an instrumental resolution of 2.8 cm^{-1}. The measurements were performed in the transmission mode over the range 2.5 μm - 25 μm. Transmission through the sample was normalized to the signal obtained in the absence of sample.

Results and Discussion

Smooth and homogeneous zinc sulfide films have been prepared on both silicon and silica substrates by conversion of zinc oxide films prepared by an ultrasonic nebulization and pyrolysis technique. The films of ZnS varied in thickness from 0.1 μm to 1 μm and the thickness was uniform to within 1% as indicated by ellipsometry measurements. These films had good adherence to both substrates. They appeared uniform and shiny with bright colors varying with the thickness. There was little difference in the quality of the initial zinc oxide and final zinc sulfide films.

X-ray diffraction analysis was used to determine the appropriate conditions for the conversion. It was desired that the conversion should be carried out at the lowest possible temperature, provided the reaction can be completed. It was found that after annealing in H_2S at 430°C for 1 1/2 hrs, a film of 1μm thickness still contained a large amount of zinc oxide. The peaks of ZnO disappeared in patterns of such films after an anneal was performed at 500°C for 3 hrs in H_2S. No impurity phase could be detected.

X-ray diffraction analysis was performed on the zinc sulfide films as deposited on the substrates. The diffraction patterns showed that the films consisted of ZnS crystallized as a mixture of cubic and hexagonal phases. Both structures consist of close-packed sulfur planes with zinc atoms occupying half of the tetrahedral sites. The only difference between them is in the stacking sequence of the anion planes. Hexagonal zinc sulfide films can therefore partially convert to the more stable cubic zinc sulfide form under the conditions of film preparation. This apparently occurs without any appreciable reduction in the quality of the final film which is formed. Two phase zinc sulfide films have also been reported by previous investigators (9).

The prepared zinc sulfide films were examined with scanning electron microscopy. They showed a uniform grain texture and the particle size grew larger with thicker films. This is similar to the properties of the precursor zinc oxide films (8). Fig. 1 shows a picture of a film with a thickness of 1 μm. The surface of the film showed a submicron grain texture with the size of most particles being about 0.3 μm. Some films were analyzed with EDS. The results confirm the presence of ZnS with 50.2 atomic percent zinc and 49.8 atomic percent sulfur.

ZnS films have been found suitable as single-layer antireflection coatings in the region from 8 to 15 μm (10). For the ZnS films deposited in this study onto silicon, infrared spectroscopic measurements were performed. Fig. 2 shows the measured transmittance of a 0.5 mm thick silicon wafer uncoated and coated with a single layer of ZnS of 1.15 μm on each side. The transmittance at 10 μm ($n_1 d_1 = \lambda/4$) is increased from 50 to 86% and remains above 70% from 7.3 μm to 15 μm. The maximum transmittance for such a sample can be calculated to be 93% at λ = 10 μm (11). Thus the antireflection performance of our ZnS films was close to the theoretical value.

Fig. 3 shows the infrared spectra of zinc oxide and zinc sulfide films on silicon substrates in the range from 200 cm^{-1} to 600 cm^{-1}. The strong band of the principal lattice absorption can be clearly seen at 280 cm^{-1}. Zinc oxide films have a broad absorption band with the peak at 410 cm^{-1}, which is consistent with Collins' results obtained from the reflectivity of a zinc oxide single crystal (12). The peak position of the absorption band of the zinc sulfide films was at 278 cm^{-1}. Kwasniewski (13) reported a broad absorption band covering 250 - 355 cm^{-1} in the infrared transmission spectrum of cubic ZnS. Detailed information near the peak was not given because single crystals were used that were much thicker than thin films. Brafman (14) reported that the fundamental resonance frequencies of zinc sulfide with the hexagonal and cubic structures were 273 and 276 cm^{-1}, respectively, which is verified by the

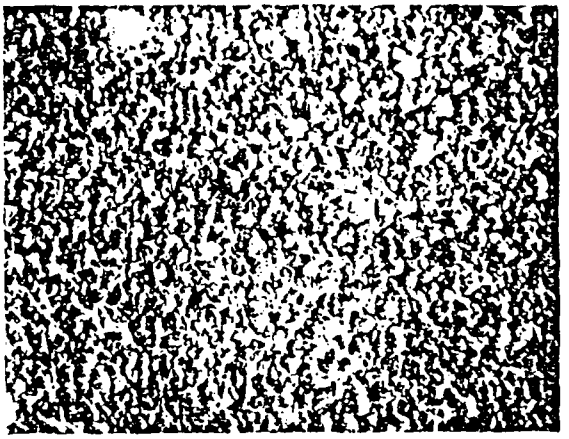

Fig. 1. Photomicrograph of a zinc sulfide film with a measured thickness of 1 μm. The grains average 0.3 μm in diameter.

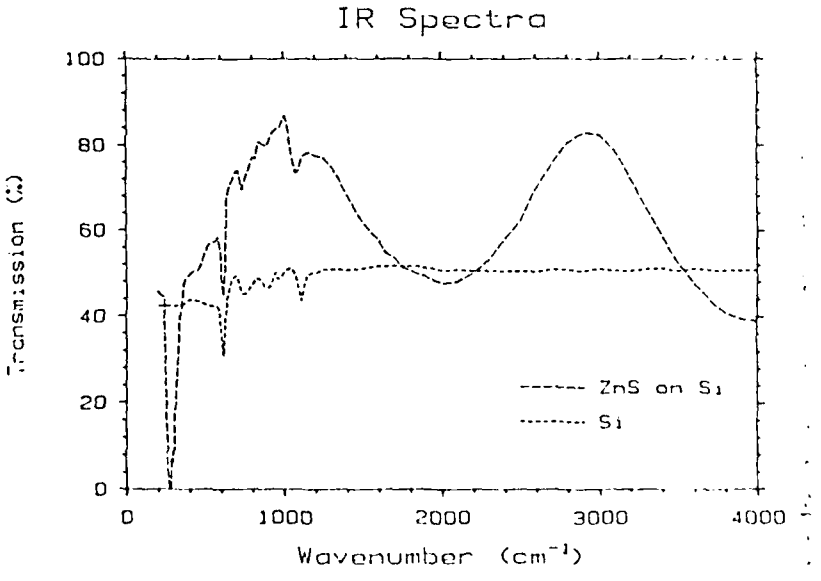

Fig. 2. Transmission spectrum of a silicon wafter 0.5 μm thick coated with a 1.15 μm layer of ZnS on each side.

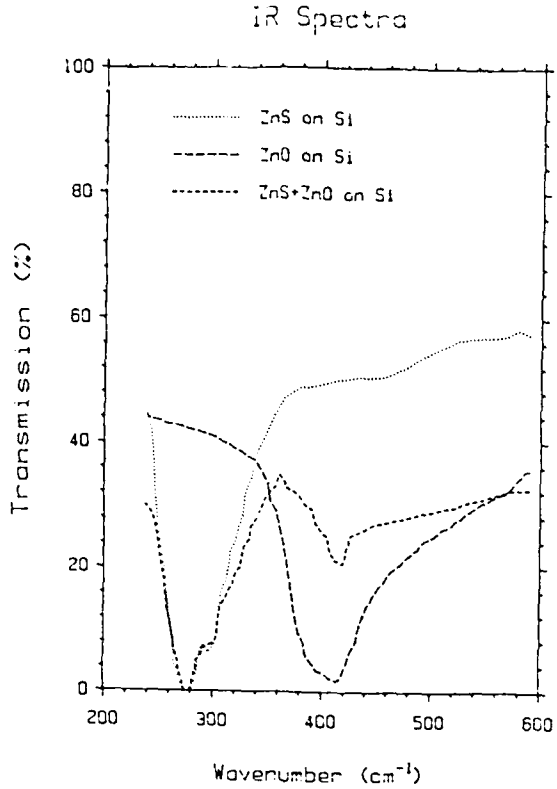

Fig. 3. Comparative infrared spectra of films of untreated zinc oxide, zinc oxide partially coverted to the sulfide, and of fully converted zinc sulfide.

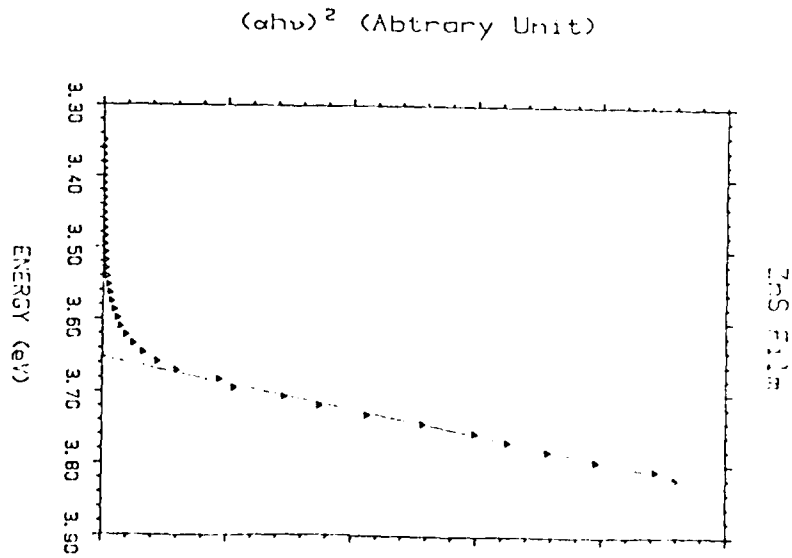

Fig. 4. Determination of the direct optical band gap of zinc sulfide.

recent work of Memon (15). These results are all consistent with the results obtained in this investigation. Infrared spectra of zinc sulfide films was used as a means of verifying the completion of conversion of ZnO to ZnS. It is shown in Fig. 3 that a film partially converted to sulfide has both absorption band characteristics of zinc sulfide and zinc oxide.

The optical transmission of zinc sulfide films on silica substrates was measured and the transmission near the absorption edge was used to generate the plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$ as shown in Fig. 4. The intercept of the plot gave the energy of the direct band gap. It was found that the direct band gap of the prepared zinc sulfide films was 3.65 eV, which is consistent with the value given in the literature (4).

Conclusions

This study has demonstrated the preparation of zinc sulfide films by the conversion of zinc oxide films to zinc sulfide in the presence of H_2S. Zinc oxide films were prepared as a precursor by ultrasonic nebulization of zinc acetate solution followed by decomposition of the zinc acetate to zinc oxide. Uniform films of ZnS with good adherence have been obtained using this technique. The transparent polycrystalline films have submicron grain texture with a bandgap of 3.65 eV. They showed potential as an IR antireflection coating material.

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